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Electron-Vibration Interactions in Carrier-Transport Material: Vibronic Coupling Density Analysis in TPD

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Abstract

Vibronic coupling, or electron-vibration coupling constant in N,N' -diphenyl- N,N' -di(m-tolyl)benzidine (TPD) cation is calculated from vibronic coupling integrals. The calculated constants are very small compared with other π conjugated systems. The calculated constants are analyzed on the basis of vibronic coupling density (VCD). The VCD analysis clearly reveals that large contributions originate from the phenyl group and tolyl group. In addition, the hole transport property of electrode-TPD molecule-electrode system is investigated using Non-equilibrium Green Function (NEGF) theory. Reflecting the small coupling, the current suppression and power loss are less than 1/2 compared with other π conjugated systems such as oligothiophenes.

I. INTRODUCTION

Hole-transport materials have been investigated as a component of multi-layer structures in organic light-emitting devices (OLED).¹⁻⁸ Aromatic amines have been employed as hole-transport materials with a high carrier mobility.⁹⁻¹³ *N,N'*-diphenyl-*N,N'*-di(m-tolyl)benzidine (TPD, Fig. 1(a)) is one of the hole-transport materials employed in the OLED.^{2,4,5,8} In 1984, Stolka *et al.* have reported that TPD/polycarbonate solid solutions have a high carrier mobility.⁹ Kaji *et al.* have observed ¹⁵N NMR spectra, and compared with their density functional calculations.¹³ They have found that a TPD molecule in the amorphous phase is similar in geometry to the free molecule.

A high carrier mobility and a low power loss are required in the development of carrier transport materials in OLED. A mobility measurement on TPD has revealed that the hole transport in this material can be described by the simple disorder-controlled hopping model without a polaron formation.¹⁰ Sakanoue *et al.* have obtained the small reorganization energy of an aromatic amine, triphenyl amine (TPA), based on the Marcus theory employing theoretical calculations.¹²

One of the important factors determining these properties is a vibronic coupling, or electron-vibration interaction. Small vibronic couplings in a molecule should result in a high mobility, a small reorganization energy,^{12,14} and a low power loss, in other words, a low heat dissipation. It is one of the necessary conditions for hole-transport materials that a molecule has small intramolecular vibronic couplings. To design efficient hole-transport materials in a molecular level, we should elucidate the reason why aromatic amines such as TPD have small vibronic coupling constants (VCC). Sato *et al.* have proposed a new method of the calculation for VCC and a concept of vibronic coupling density (VCD) which

enables us to analyze the calculated result on the basis of the electronic and vibrational structures.^{15–18}

Recently theoretical calculations of carrier transport through a single molecule including the electron-molecular vibration interaction have been reported based on the non-equilibrium Green's function (NEGF) theory.¹⁹

In this Letter, we address the reason of the small couplings in TPD employing the VCD analysis and calculate a current suppression through a single TPD molecule due to the vibronic coupling based on the NEGF theory.

II. METHOD OF CALCULATION

The electronic and vibrational structures were calculated using GAMESS.²⁰ We adopted the calculation method for the VCC and VCD described in our previous paper.¹⁸ The optimized structure \mathbf{R}_0 and vibrational structure of the neutral molecule were calculated using restricted Hartree-Fock (RHF) method with 6-31G basis set including the first derivatives which ensure the Hellmann-Feynman theorem applicable in the calculation. Vibronic coupling constants V_i of the vibrational mode i were calculated from vibronic integrals:

$$V_i = \left\langle \Phi_{N-1}(\mathbf{r}, \mathbf{R}_0) \left| \left(\frac{\partial U}{\partial Q_i} \right)_{\mathbf{R}_0} \right| \Phi_{N-1}(\mathbf{r}, \mathbf{R}_0) \right\rangle, \quad (1)$$

where Φ_{N-1} is a restricted open Hartree-Fock (ROHF) wavefunction of the ionized state with $N - 1$ electrons at the equilibrium configuration \mathbf{R}_0 of the neutral molecule, Q_i normal coordinate, U potential, and

$$\left(\frac{\partial U}{\partial Q_i} \right)_{\mathbf{R}_0}$$

is the electronic part of the vibronic coupling operator:

$$\left(\frac{\partial U}{\partial Q_i} \right)_{\mathbf{R}_0} Q_i$$

appearing in the Hertzberg-Teller expansion.²¹ In the present calculation, orbitals should have a correct symmetry. The ROHF method is appropriate since unrestricted methods such as UHF and UB3LYP yield orbitals with a broken symmetry.¹⁵

Vibronic coupling density $\eta_i(\mathbf{x})$ is defined by

$$\eta_i(\mathbf{x}) = \Delta\rho(\mathbf{x}) v_i(\mathbf{x}), \quad (2)$$

where $\Delta\rho(\mathbf{x})$ is an electron density difference between the neutral and ionized state

$$\Delta\rho(\mathbf{x}) = \rho_+(\mathbf{x}) - \rho_0(\mathbf{x}), \quad (3)$$

and $\mathbf{x} = (x, y, z)$. For comparison, frozen density difference is defined using the HOMO ψ_{HOMO} of the neutral molecule by

$$\Delta\rho_{\text{F}}(\mathbf{x}) = -\psi_{\text{HOMO}}^*(\mathbf{x})\psi_{\text{HOMO}}(\mathbf{x}). \quad (4)$$

The density difference defined in Eq. (3) is called relaxed density difference $\Delta\rho_R$. $v_i(\mathbf{x})$ denotes a potential derivative with respect to a normal coordinate Q_i :

$$v_i(\mathbf{x}) = \sum_{\mu} \left[\frac{\partial}{\partial Q_i} \frac{Z_{\mu}}{|\mathbf{x} - \mathbf{X}_{\mu}|} \right]_{\mathbf{R}_0}, \quad (5)$$

where $\mathbf{X}_{\mu} = (X_{\mu}, Y_{\mu}, Z_{\mu})$ denotes the Cartesian coordinate of nucleus μ . Note that v_i is a one-electron operator. The vibronic coupling density gives a local map of the interaction, since the integration of $\eta_i(\mathbf{x})$ over the whole space yields the vibronic coupling constant V_i :

$$V_i = \int \eta_i(\mathbf{x}) d\mathbf{x}. \quad (6)$$

Orbital vibronic coupling constant of molecular orbital k for vibrational mode i is defined by

$$\beta_{ik} = \langle \psi_k(\mathbf{x}) | v_i(\mathbf{x}) | \psi_k(\mathbf{x}) \rangle. \quad (7)$$

The Sum of β_{ik} over the occupied orbitals yields the electronic component of the vibronic coupling constant V_i in the Hartree-Fock approximation. Atomic vibronic coupling constant $\alpha_{i\mu}$ of atom μ for vibrational mode i is defined by

$$\alpha_{i\mu} = \left(\sum_{k \in \text{occ}} \left\langle \psi_k(\mathbf{x}) \left| \left\{ \nabla_{\mu} \left(-\frac{Z_{\mu}}{|\mathbf{x} - \mathbf{X}_{\mu}|} \right) \right\} \right| \psi_k(\mathbf{x}) \right\rangle + \sum_{\nu} \left\{ \nabla_{\mu} \left(-\frac{Z_{\nu} Z_{\mu}}{|\mathbf{X}_{\nu} - \mathbf{X}_{\mu}|} \right) \right\}_{\mathbf{R}_0} \right) \cdot \frac{\mathbf{u}_{\mu}^i}{\sqrt{M_{\mu}}}, \quad (8)$$

where \mathbf{u}_{μ}^i is the μ component of a vibrational vector in mass-weighted coordinates and M_{μ} the mass of atom μ . Within the Hartree-Fock approximation, the sum of $\alpha_{i\mu}$ over the atoms also yields the electronic component of the vibronic coupling constant V_i . The atomic vibronic coupling constant $\alpha_{i\mu}$ indicates a contribution of the atom μ to the vibronic coupling of the mode i .

Transport properties were calculated based on Ref. 19.

III. RESULTS AND DISCUSSION

We obtained a C_2 structure as an optimized structure, and performed vibrational analysis for the C_2 structure to confirm that it is a minimum. Since the electronic structure has no degeneracy, only the a_g vibrational modes have a non-zero vibronic coupling. Couplings of b_g modes are zero because of the symmetry. Figure 1 (b) shows the calculated vibronic coupling constant of the a_g modes. Vibrational modes with the strong coupling and their assignment are tabulated in Table 1. The order of the strongest one is at most of 10^{-5} a.u. which is smaller than those of typical π conjugated systems such as oligothiophenes and oligoynes by one order.²² Relatively strong couplings occur bending modes around 735 cm^{-1} and 1326 cm^{-1} . The strongest coupling mode is depicted in Fig. 1 (c). We concentrate ourselves on the strongest mode shown in Fig. 1 (c).

Though the mode shown in Fig. 1(c) is the strongest in TPD cation, order of the coupling is small compared with other π conjugated systems by one order. The reason can be realized with the aid of the vibronic coupling density which yields a local map of a vibronic coupling on the basis of the electron density difference $\Delta\rho$ and the potential derivative v_i .

The potential derivative v_i of the strongest mode is shown in Fig. 2. Reflecting the vibrational vector of the mode, v_i takes large values on the phenyl, tolyl groups, and the nitrogen atoms. Figure 3 (a) shows the relaxed electron density difference $\Delta\rho_R$. We can see that the electron density difference greatly lies on the nitrogen atoms, and small portion resides on the phenyl and tolyl groups.

Vibronic coupling density is defined as a product of $\Delta\rho$ and v_i . Electron density difference is also related to geometry change via vibronic coupling. The structural change upon oxidation in organic molecules has been discussed^{23,24} The vibronic coupling density η_R of the strongest mode is shown in Fig. 3 (b). It should be noted that the coupling density is localized mostly on the nitrogen atoms. However, since the coupling density is distributed symmetrically around the nitrogen atoms with the positive and negative signs, the contribution near the nitrogen atoms to the coupling constant is quite small. On the other hand, since $\Delta\rho$ is distributed asymmetrically on the phenyl and the tolyl groups, the coupling density is distributed in an asymmetric manner with a little cancellation. Thus, the coupling density on these groups greatly contributes to the vibronic coupling. In Table 2, atomic vibronic coupling constant and their summation over the groups are tabulated. It is found that the main contribution originates from the phenyl and the tolyl groups. The electron density difference which is symmetrically localized on the nitrogen affords a little contribution to the vibronic coupling. This is the reason why the TPD cation has the small vibronic couplings.

Figures 4 show (a) the frozen electron density difference $\Delta\rho_F$ and (b) vibronic coupling density η_F employing $\Delta\rho_F$. It is found that the density difference and the coupling density reside on the phenylene group, which is completely different from the results obtained from $\Delta\rho_R$. This means that we cannot discuss vibronic coupling on the basis of a frontier orbital only. The use of relaxed density is crucial in the calculation of vibronic coupling.¹⁸

The calculated $I - V$ characteristics and the power loss are shown in Figs. 5(a) and (b). Note that we do not intend to simulate an $I - V$ characteristics observed in bulk systems. Our interest lies in a suppression effect on current due to the electron-vibration interaction in the TPD molecule. The suppression of the current and the power loss is less than 1/2 compared with other π conjugated systems such as oligothiophenes.²² This could be one of the reason that TPD is one of good hole-transport materials.

IV. CONCLUSION

We calculated the vibronic coupling, or electron-vibration coupling constants in N, N' -diphenyl- N, N' -di(m-tolyl)benzidine (TPD) cation from the evaluation of vibronic coupling integrals. The calculated constants were very small compared with other π conjugated systems. The calculated constants were analyzed on the basis of the vibronic coupling density (VCD). The VCD analysis clearly reveals that large contributions originate from the phenyl group and the tolyl group. The excess carrier density is accommodated on the nitrogen atoms. However, the density difference on the nitrogen atoms cannot contribute to the vibronic coupling, since the symmetric density distribution around the atoms are canceled. In addition, the hole transport property of electrode-TPD molecule-electrode system was investigated using Non-equilibrium Green Function (NEGF) theory. Reflecting the small coupling, the current suppression and power loss are less than 1/2 compared with

other π conjugated systems such as oligothiophenes.

There would be two approaches to reduce the inelastic current and power loss: one is to make the low frequency higher, and the other is to reduce the large vibronic coupling. For the latter approach, the vibronic coupling density analysis could be helpful in the molecular design for carrier-transport materials.

Acknowledgments

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TABLE I: Vibrational modes with a strong vibronic coupling and their assignment.

Frequency(cm^{-1})	VCC(10^{-5}a.u.)	Assignment
735	7.58	phenylene in-plane bending, phenyl in-plane bending, tolyl in-plane bending, C-N stretching
820	7.01	phenylene in-plane bending, phenyl C-H out-of-plane bending, tolyl in-plane bending
856	7.17	phenylene in-plane bending, phenyl C-H out-of-plane bending, tolyl C-H out-of-plane bending bending
1326	7.45	phenylene ring stretching, phenyl C-H in-plane bending, tolyl C-H in-plane bending, C-N stretching

TABLE II: Atomic vibronic coupling constant in 10^{-5} a.u. The numbers of the atoms are defined in FIG. 1(a).

Phenylene		Phenyl	Tolyl	Nitrogen
C1	0.381	C7 -0.680	C13 -0.522	N1 -0.314
C2	0.096	C8 -0.735	C14 -0.097	
C3	0.090	C9 -0.182	C15 -0.246	
C4	-0.209	C10 -0.163	C16 -0.233	
C5	0.104	C11 -0.120	C17 -0.154	
C6	0.149	C12 -0.235	C18 -0.608	
H1	0.008	H5 -0.032	C19 -0.056	
H2	0.031	H6 -0.077	H10 0.063	
H3	0.049	H7 0.060	H11 -0.041	
H4	-0.003	H8 0.001	H12 0.037	
		H9 -0.048	H13 -0.083	
			H14 0.021	
			H15 -0.024	
			H16 -0.020	
Sum	0.696	-2.211	-1.963	-0.314

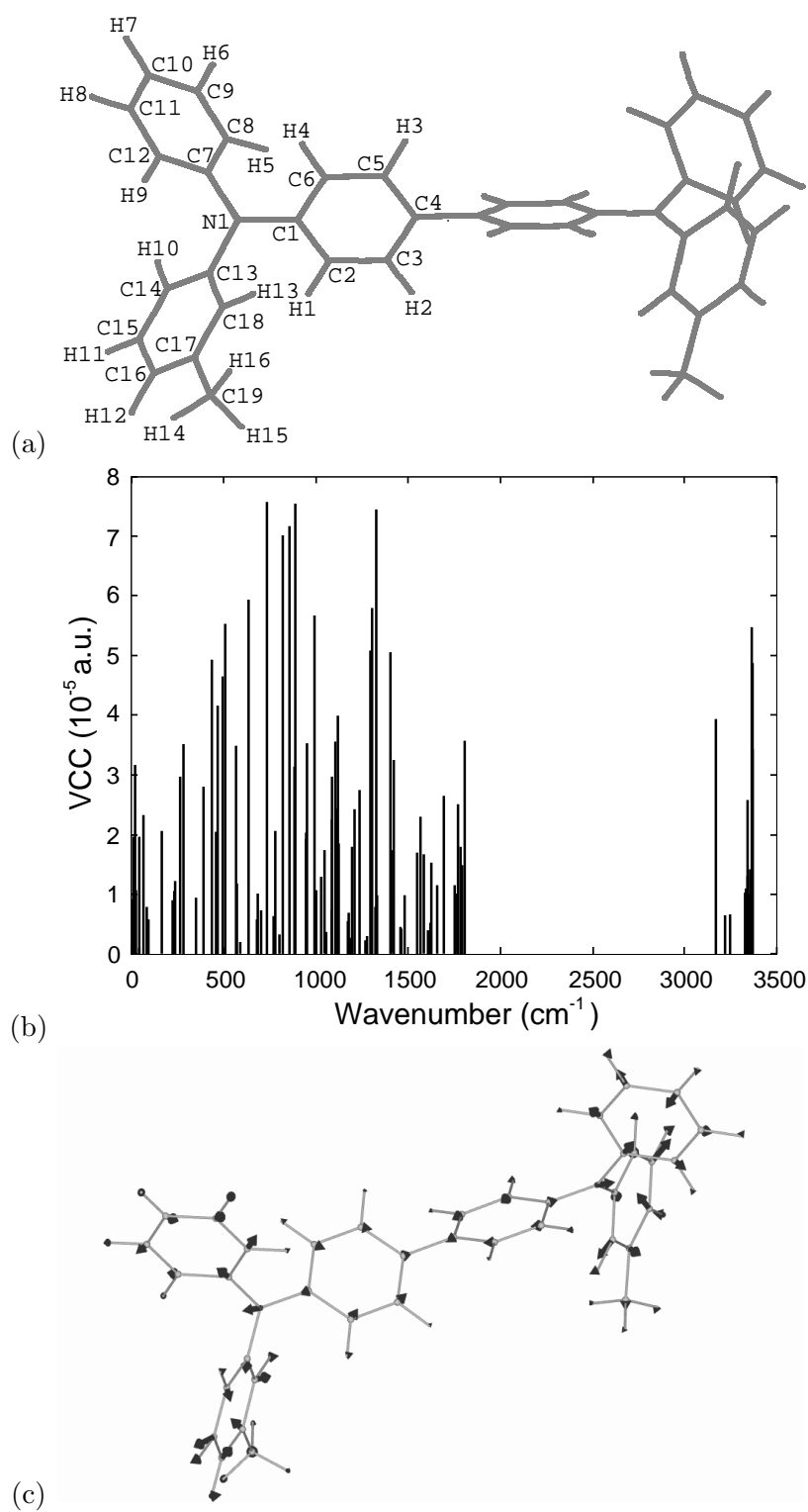


FIG. 1: Sato *et al.*

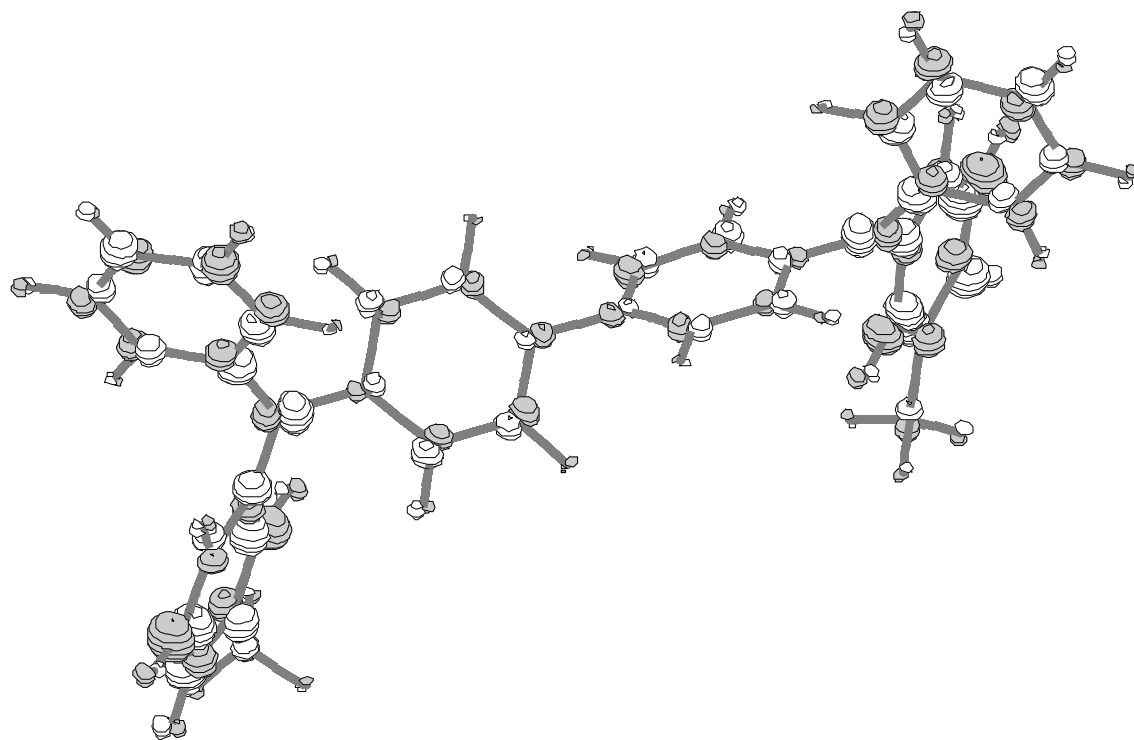


FIG. 2: Sato *et al.*

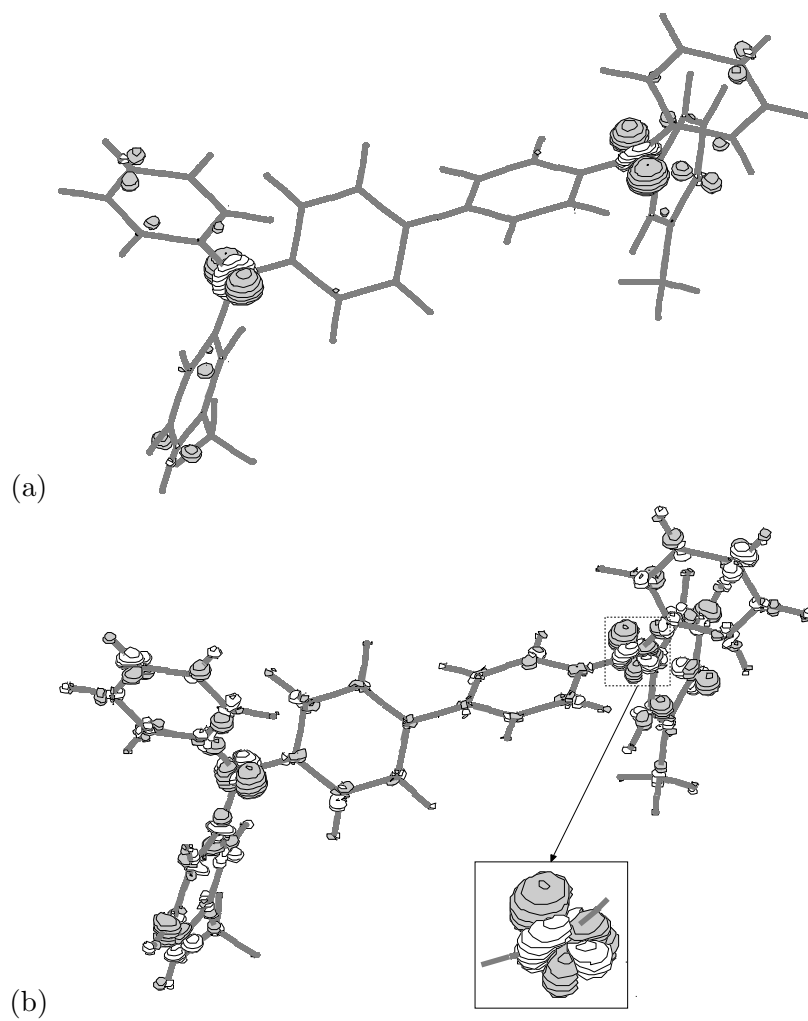


FIG. 3: Sato *et al.*

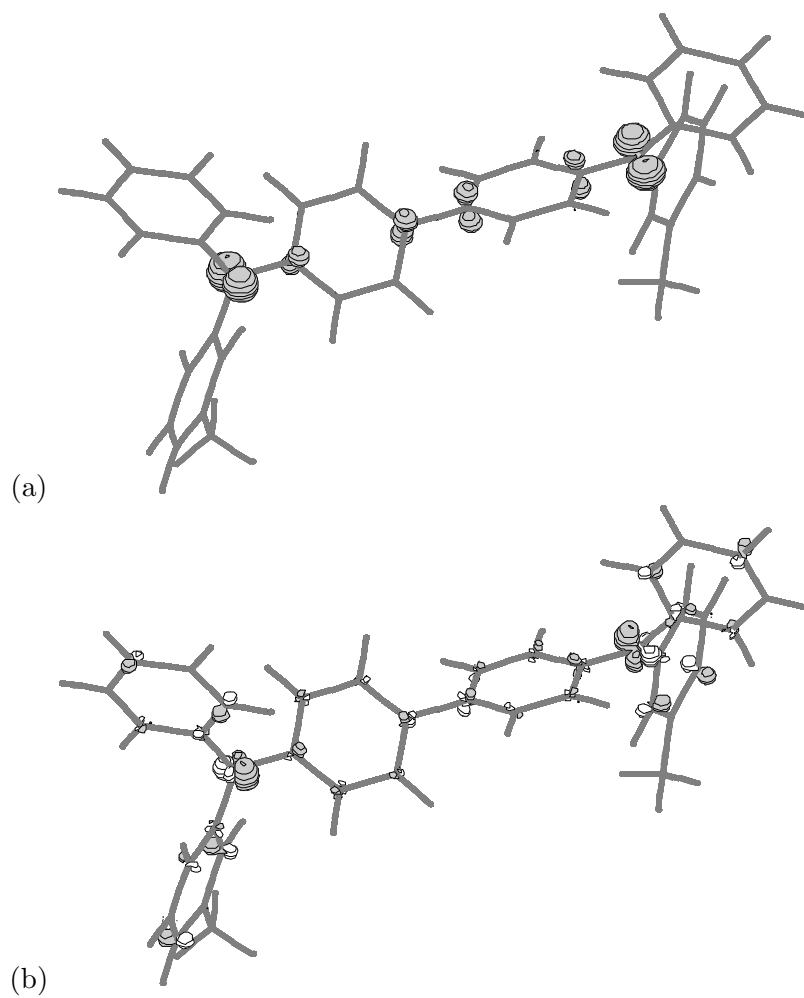


FIG. 4: Sato *et al.*

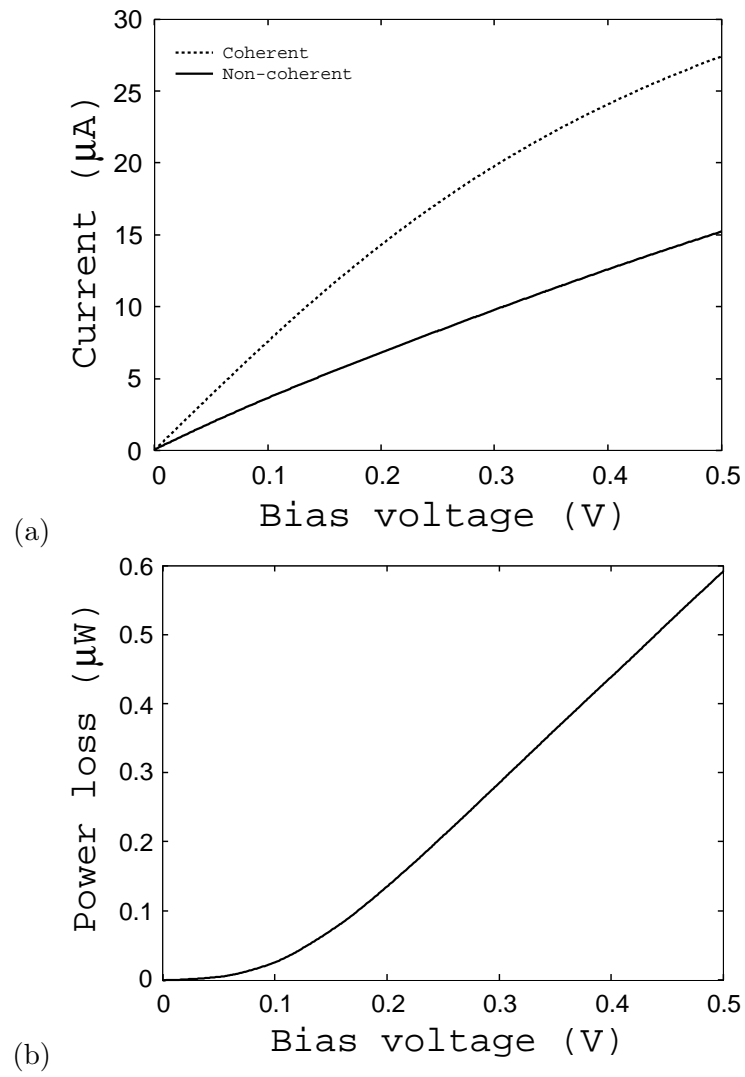


FIG. 5: Sato *et al.*

Figure captions

FIG. 1: (a) Structure of TPD, (b) calculated vibronic coupling constants, and (c) vibrational mode (735 cm^{-1}) with the strongest coupling in TPD cation.

FIG. 2: Potential derivative $v_i(\mathbf{x})$ with respect to the normal coordinate of 735 cm^{-1} mode. White is positive, and gray negative.

FIG. 3: (a) Relaxed density difference $\Delta\rho_R(\mathbf{x})$ and (b) vibronic coupling density $\eta_{iR}(\mathbf{x})$ of 735 cm^{-1} mode. White is positive, and gray negative.

FIG. 4: (a) Frozen density difference $\Delta\rho_F(\mathbf{x})$ and (b) vibronic coupling density $\eta_{iF}(\mathbf{x})$ of 735 cm^{-1} mode. White is positive, and gray negative.

FIG. 5: Transport properties through a TPD molecule. (a) $I - V$ characteristics (solid line: with the vibronic couplings, dotted line: without vibronic couplings) and (b) power loss.